

Theory and Calculation of X-Ray Absorption

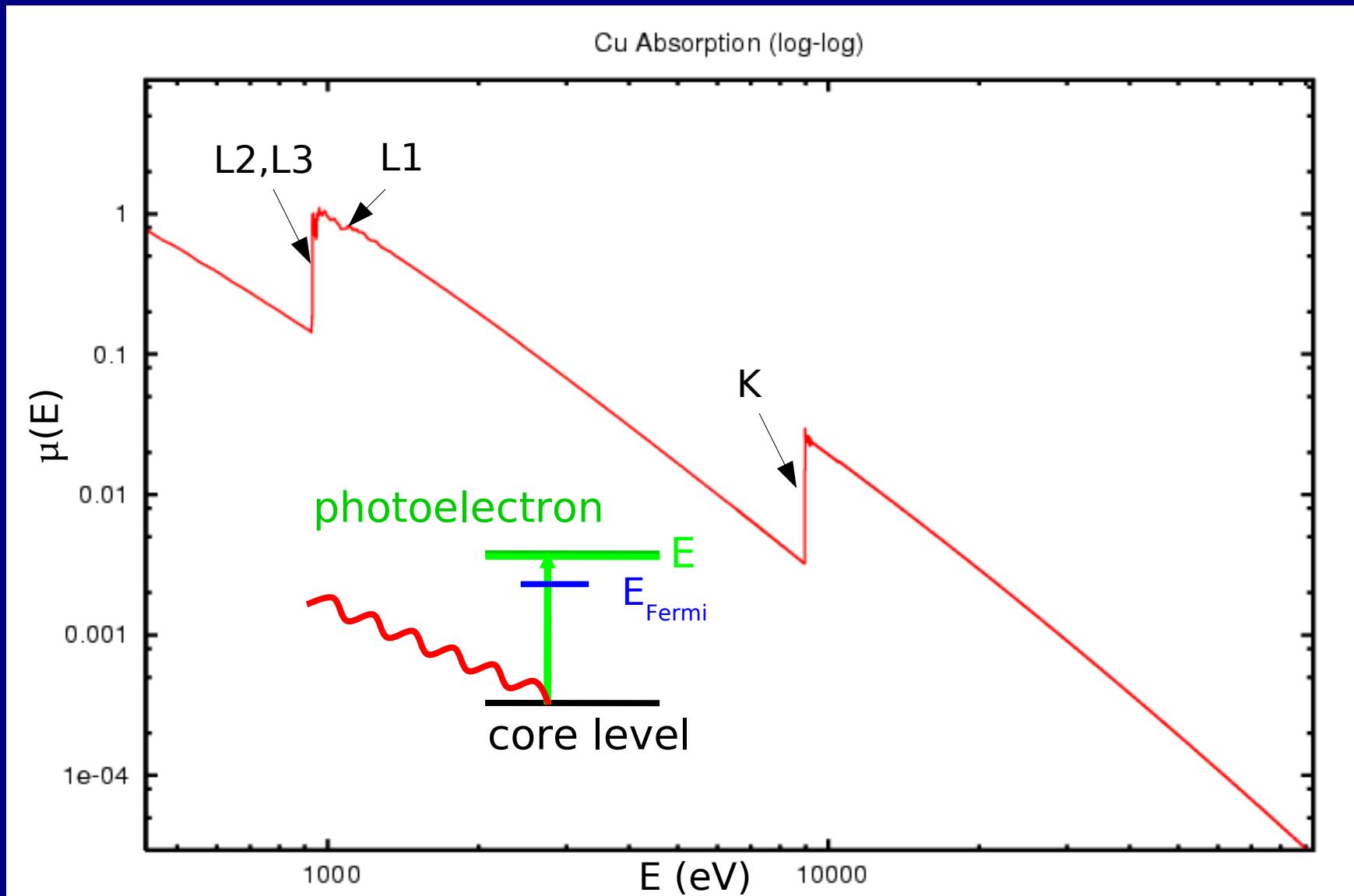
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^tSupported by NIH/SSRL, DOE and CMSN

Outline

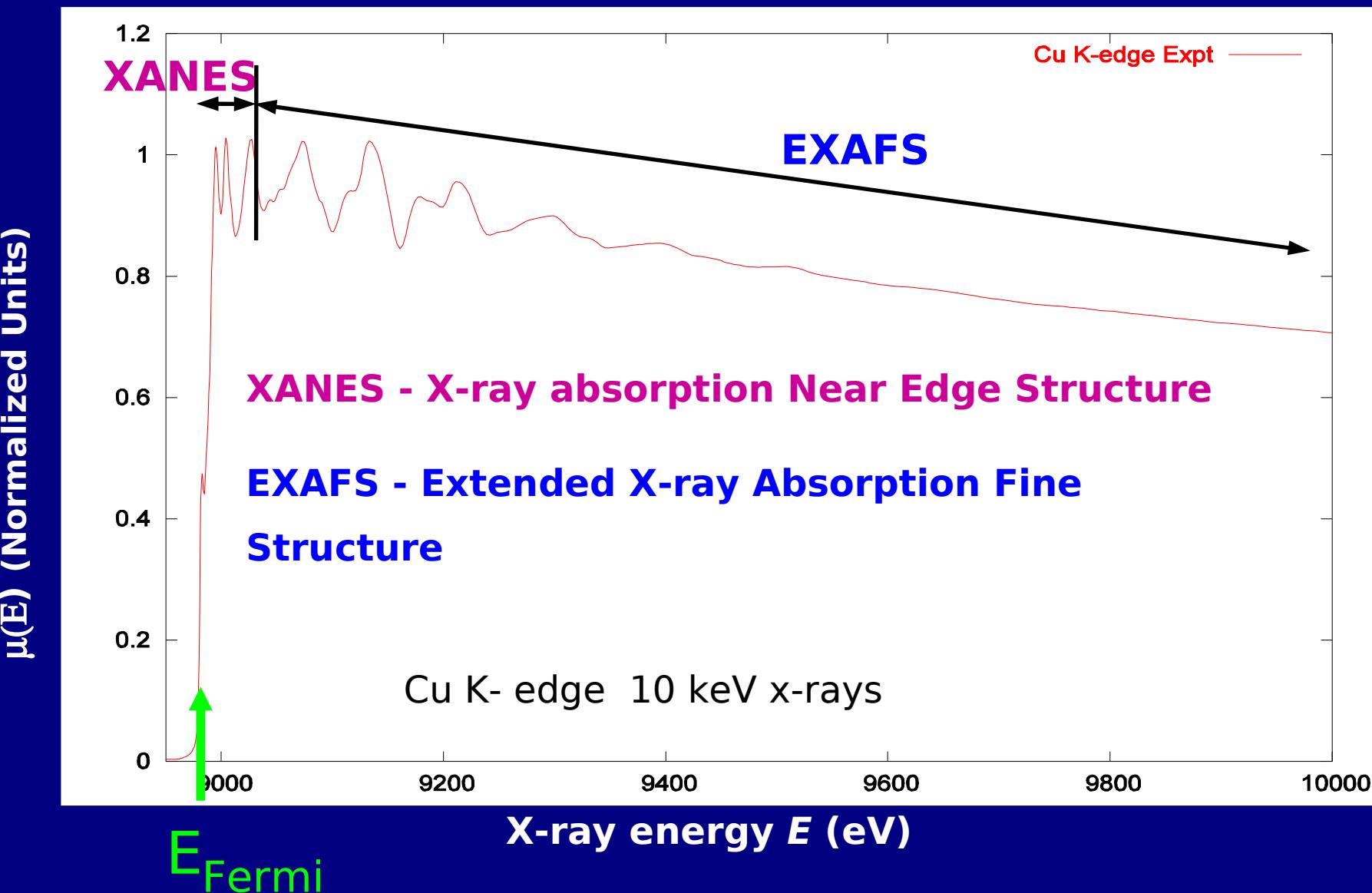
- Introduction to XAS
- Theory
 - Theory of EXAFS
 - Theory of XANES
 - L-Edge XAS and XMCD
- Calculation of XAS using FEFF
 - Calculating EXAFS
 - Calculating XANES
- The future of FEFF: FEFF9

Introduction: What is X-ray absorption?



Fine structure – EXAFS and XANES

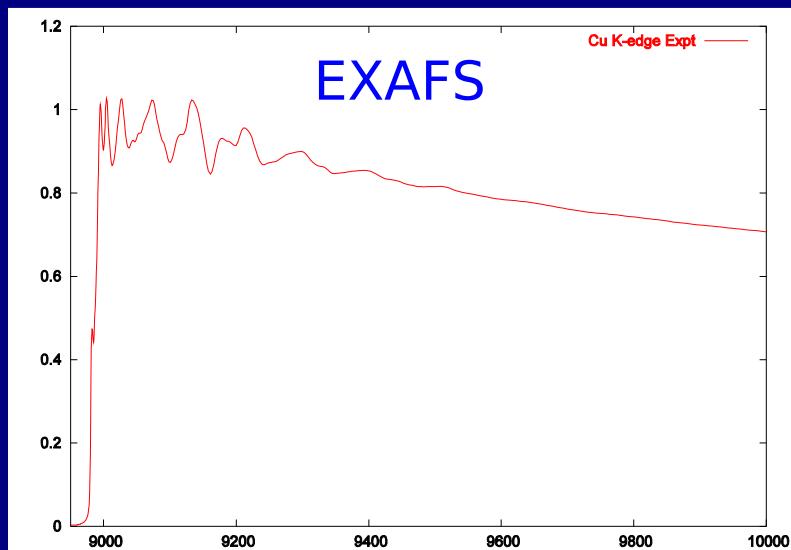
M. Newville



Qualitative Interpretation of EXAFS

D.Sayers Stern & Lytle 1970

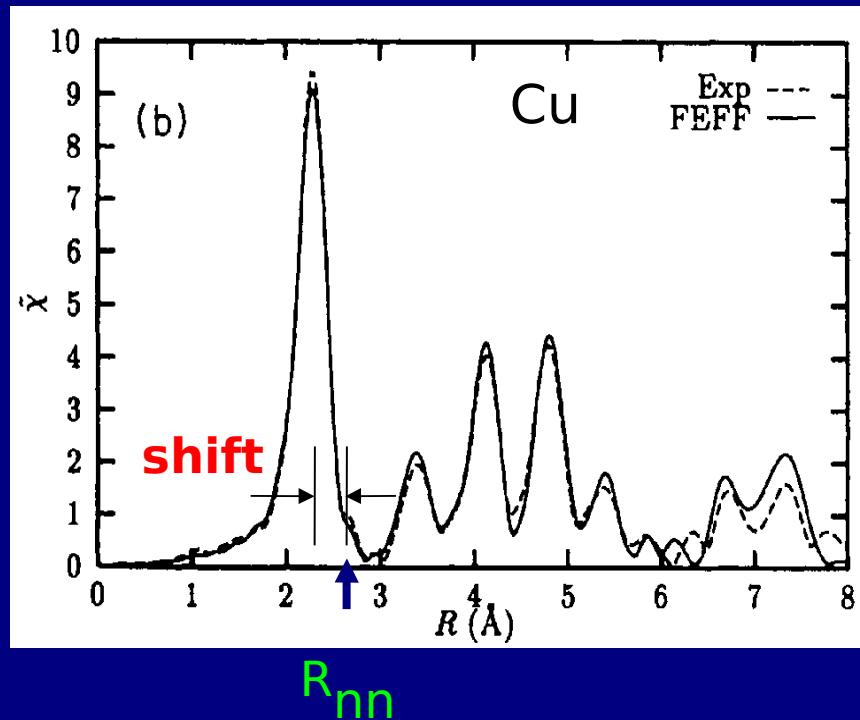
Short range order theory



→ X-ray
Microscope!

EXAFS Fourier Transform

→ **Shifted** Radial Distribution



Theory of EXAFS

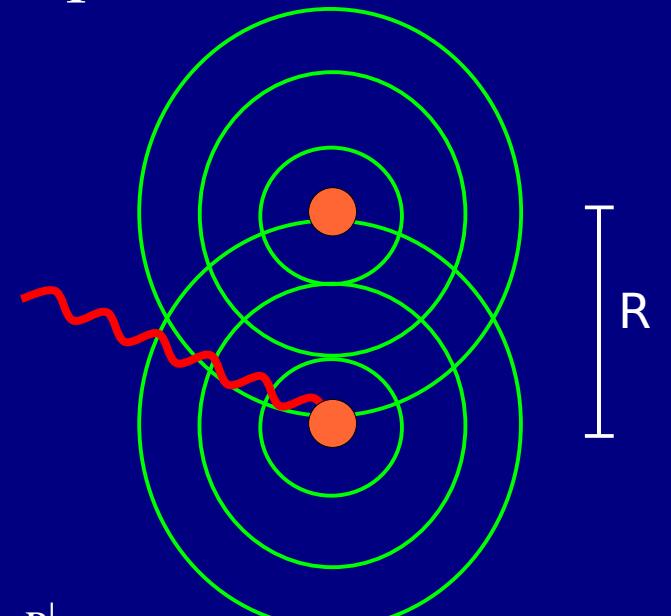
The EXAFS Equation: Heuristic Derivation

$$1) \quad \mu \propto \sum_f |\langle i | d | f \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad \text{Fermi's Golden Rule}$$

$|i\rangle$ =initial "core" state $|f\rangle$ =final "photoelectron" state

$$2) \quad \langle i | d | f \rangle \approx \psi_f(0) \int_c d^3 r \psi_i(r) \vec{\epsilon} \cdot \vec{r}$$

$$3) \quad \psi_f(r) \approx \frac{e^{ikr}}{kr} [1 + i f(\pi, k) \frac{e^{ikR}}{kR} \frac{e^{ik|r-R|}}{k|r-R|}]$$



$$4) \quad \left| \langle i | d | f \rangle \right|^2 \approx A_i [1 + i f(\pi, k) \frac{e^{ikR}}{kR} \frac{e^{ik|r-R|}}{k|r-R|} + c.c.]$$

χ is defined as the oscillatory part of the signal

$$6) \quad \chi = K f(\pi, k) \frac{\sin(2kR)}{(kR)^2}$$

Many Single Scattering events

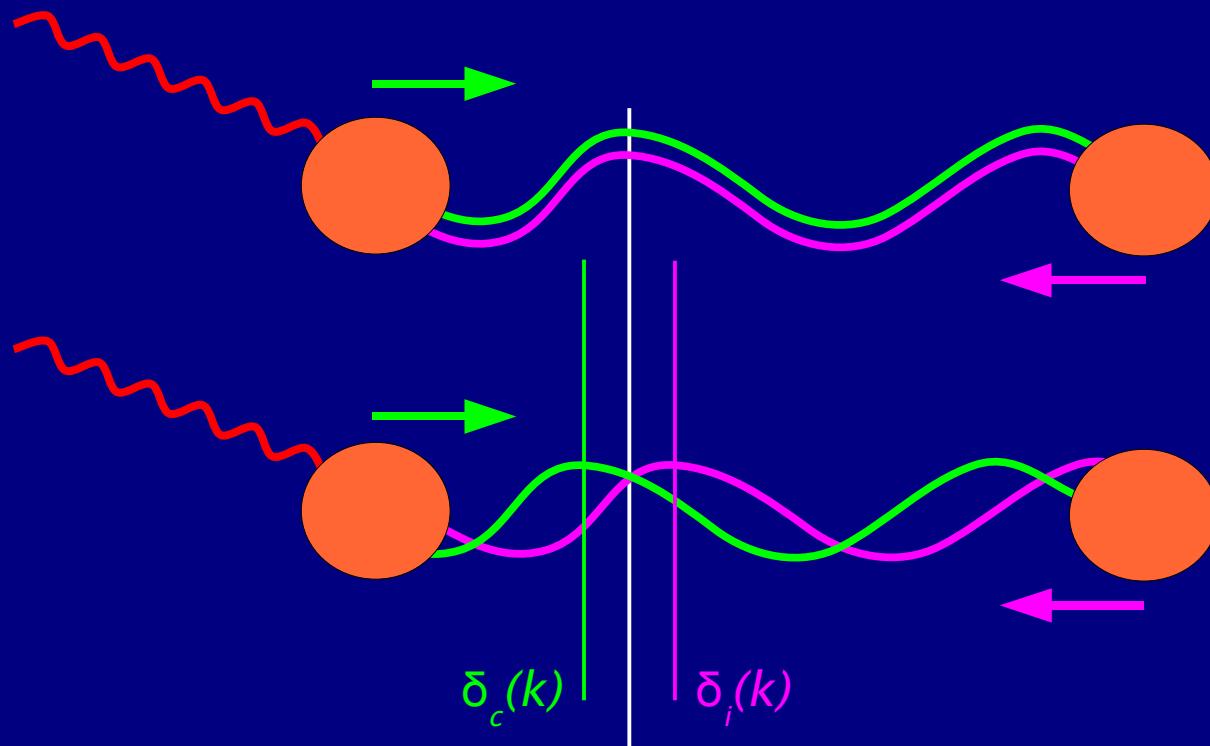
$$\Rightarrow \chi = \sum_i A_i f_i(\pi, k) \frac{\sin(2kR_i)}{(kR_i)^2}$$

The real EXAFS equation:

- Phase shifts
- Debye Waller Factors
- Inelastic Losses
- Many Body Effects - S_0^{-2}
- Multiple scattering

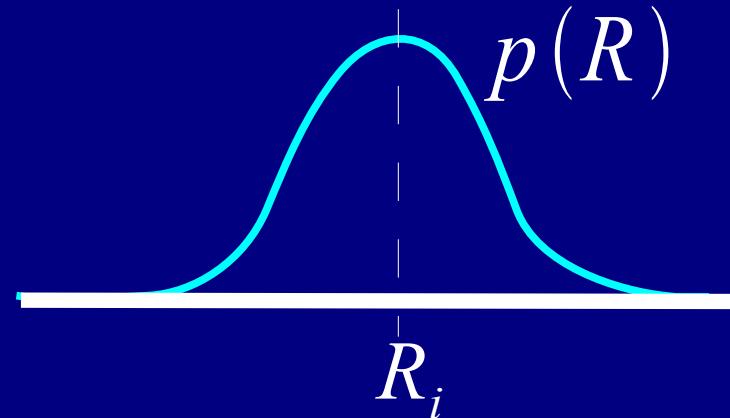
Phase Shifts

$$\Rightarrow \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2}$$

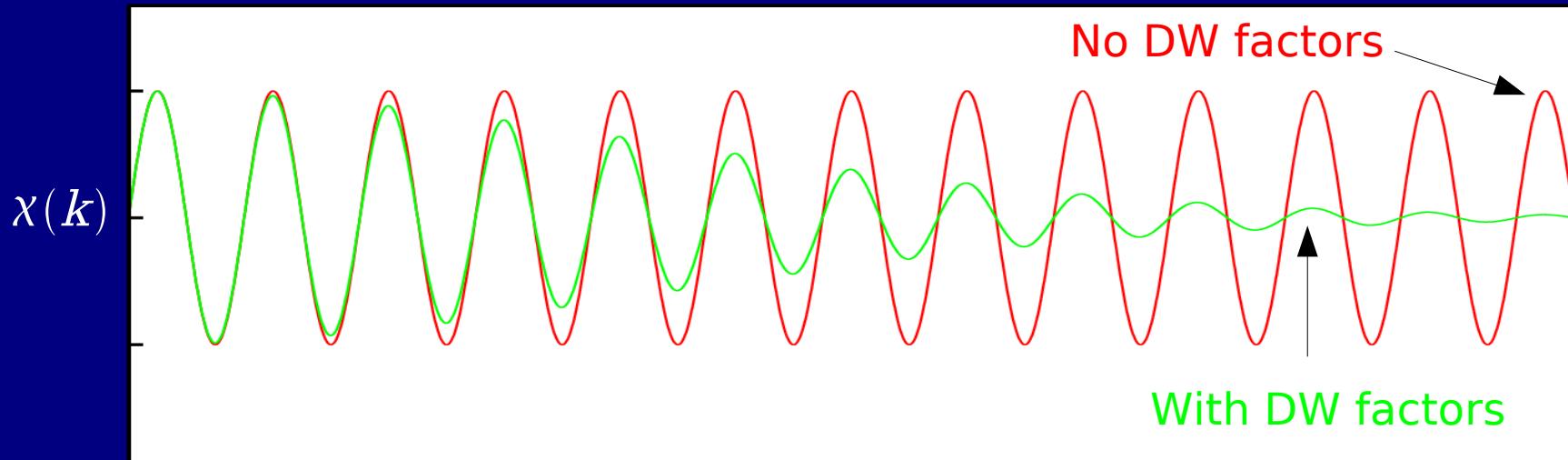


Disorder - Debye Waller factors

$$p(R) = (2\pi\sigma_i^2)^{\frac{1}{2}} e^{-\frac{(R-R_i)^2}{2\sigma_i^2}}$$



$$\Rightarrow \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \exp(-2\sigma_i^2 k^2)$$



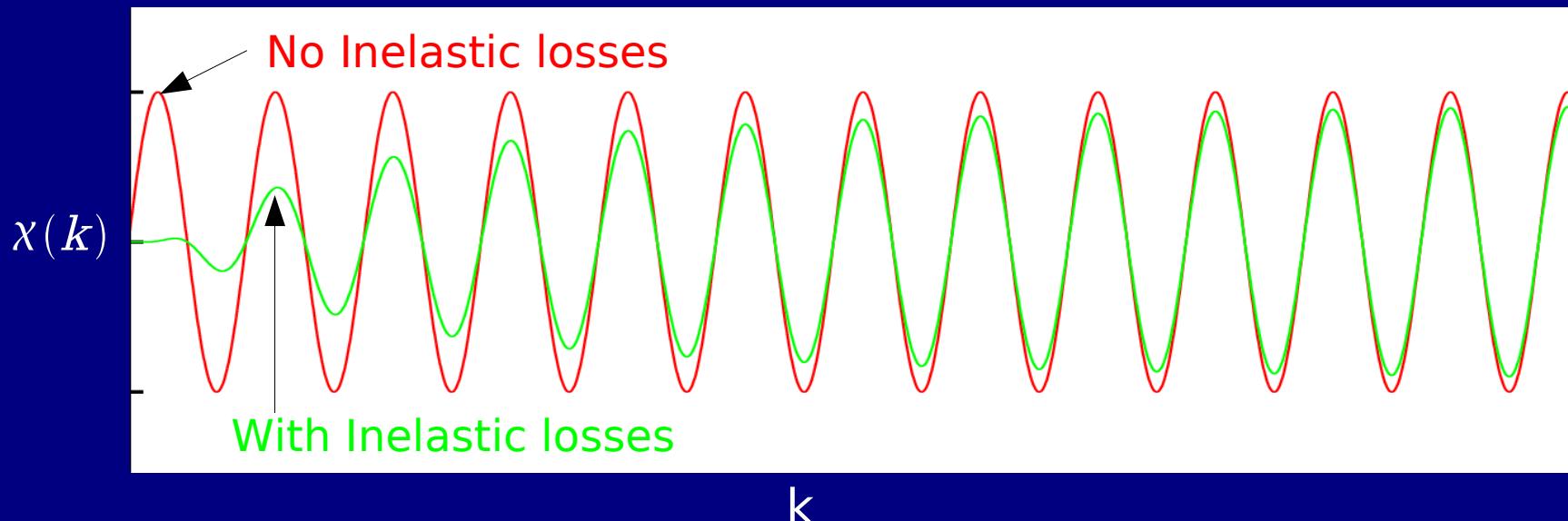
Inelastic losses

Photoelectron and core hole have finite lifetimes

$$E_{qp} = \frac{p^2}{2m} + \Sigma(E) + i\Gamma_{ch} \quad p_{qp} = p' + ip'' = p' + \frac{i}{\lambda}$$

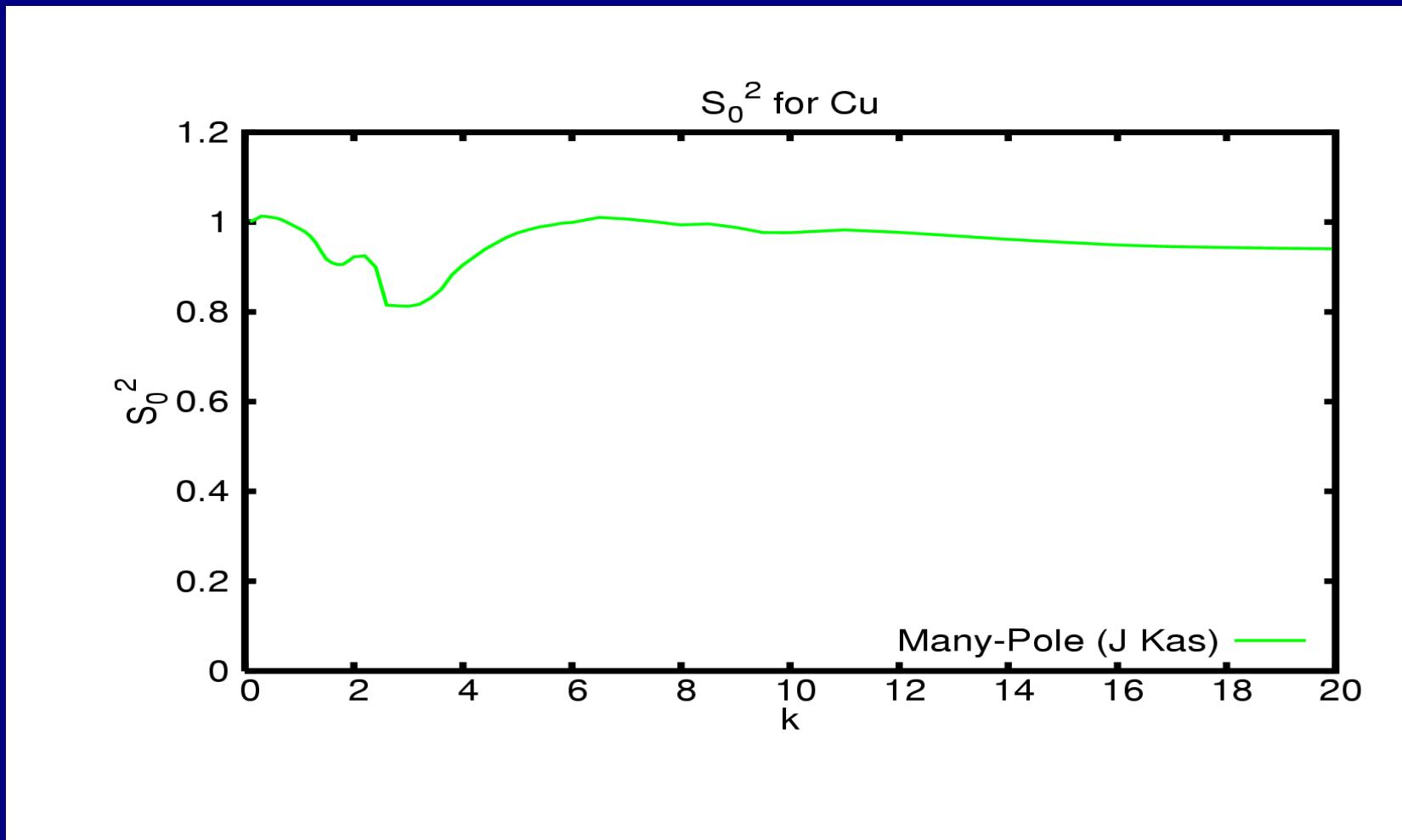
$$\lambda \approx \frac{k}{|\text{Im } \Sigma| + \Gamma_{ch}}$$

$$\Rightarrow \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \exp\left(\frac{-R}{\lambda(k)}\right)$$



Many Body Effects - S_0^2

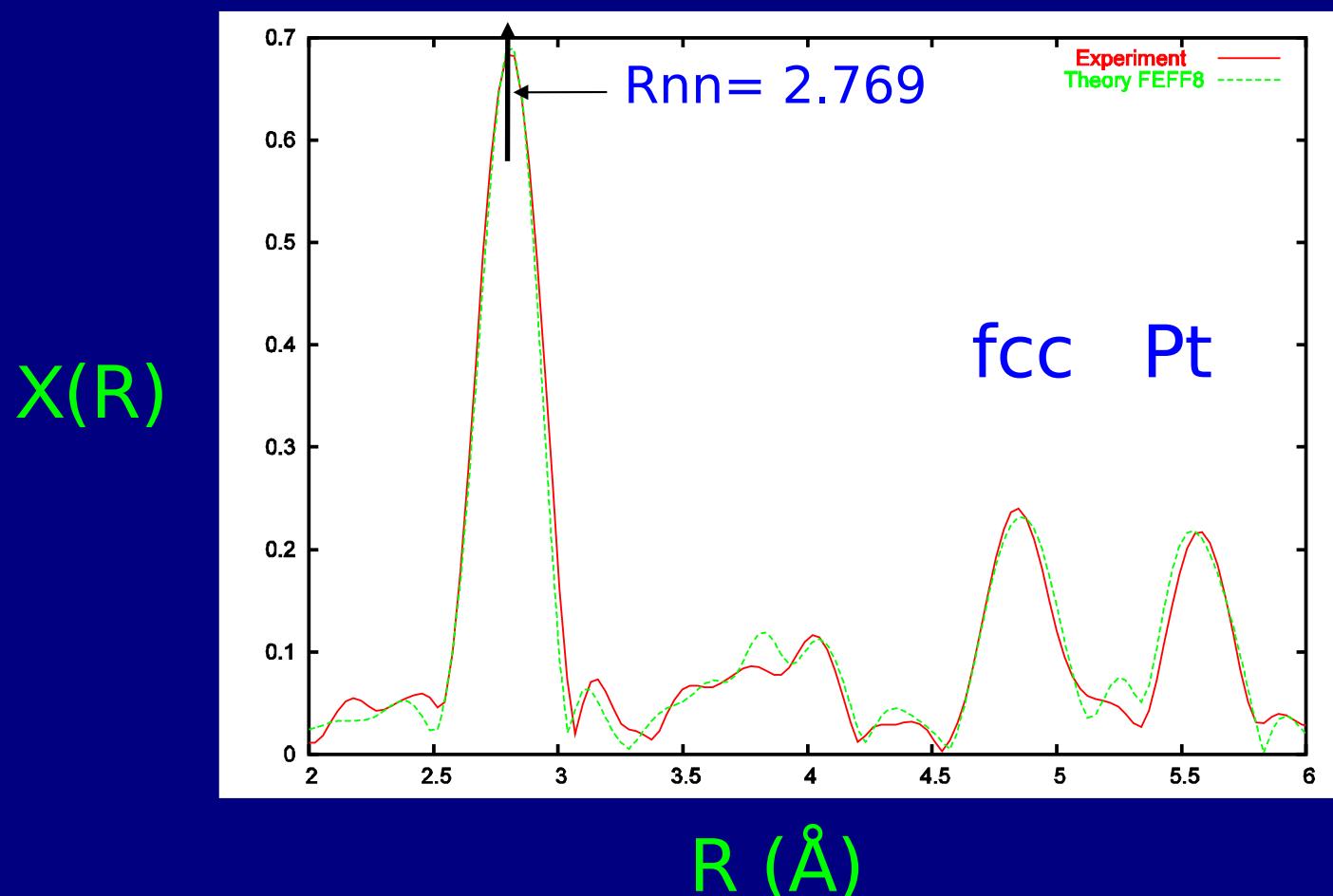
$$\Rightarrow \chi = \sum_i N_i S_0^2 |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} e^{\frac{-R}{\lambda(k)}}$$



Multiple scattering and curved wave scattering amplitudes

$$\chi = \sum_i N_i S_0^2(k) \left| f_{eff}^i(\pi, k) \right| \frac{\sin((2kR_i + \delta_c(k) + \delta_i(k)))}{(kR_i)^2} e^{\frac{-R}{\lambda(k)}} e^{-2k^2\sigma^2}$$

Phase corrected EXAFS Fourier transform –
radial distribution function



X-Ray Absorption

Principles, Applications, Techniques of EXAFS, SEXAFS and XANES

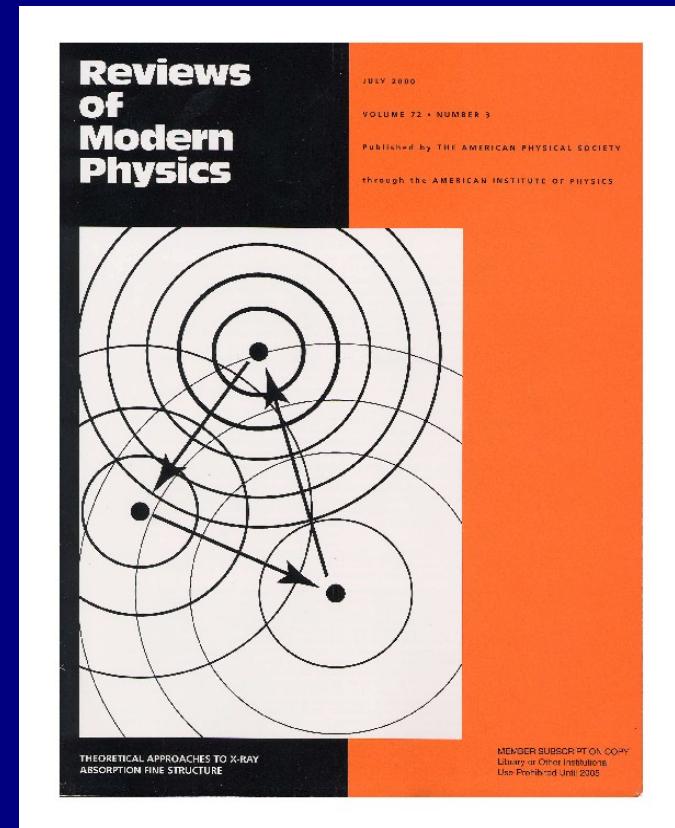
Edited by Koningsberger and Prins (1988)

Chapter 1 - Theory of EXAFS, E. A. Stern

Quantitative Theory of EXAFS

J. J. Rehr & R.C. Albers

Rev. Mod. Phys. **72**, 621 (2000)



Theory of XANES

- Absorption in terms of the Green's function
- Path Expansion VS Full Multiple Scattering
- LDOS – Angular momentum projected density of states
- Symmetry and XANES
- Edge position and oxidation state/charge transfer
- L-Edges and XMCD

Green's Functions and Absorption

$$1) \quad \mu \propto \sum_f |\langle i | d | f \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad \text{Fermi's Golden Rule}$$

$$2) \quad \sum_f |\langle i | d | f \rangle|^2 \delta(E_f - E_i - \hbar\omega) = \\ \underbrace{\left\langle i \left| d \sum_f |f\rangle\langle f| \delta(E_f - E_i - \hbar\omega) d^\dagger \right| i \right\rangle}_{-\frac{1}{\pi} \text{Im } G(\omega)}$$

$$3) \quad \mu \propto -\frac{1}{\pi} \text{Im} \langle i | d G(\omega) d^\dagger | i \rangle$$

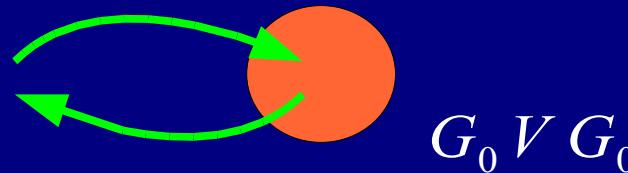
Path Expansion and Full Multiple Scattering

4) $G = [E - H_0 - V]^{-1}$

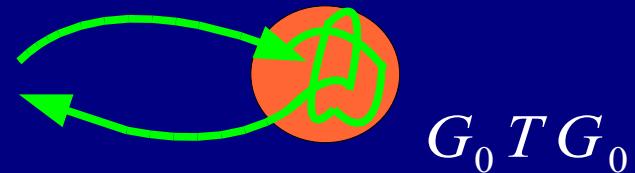
$$= [E - H_0]^{-1} \{ 1 + V(E - H_0)^{-1} + [V(E - H_0)^{-1}]^2 + \dots \}$$

5) $G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots$

G_0, T - Matrices in angular momentum and site basis



$$G_0 V G_0$$



$$G_0 T G_0$$

$\xrightarrow{\text{Path expansion}}$

$$G = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \dots$$

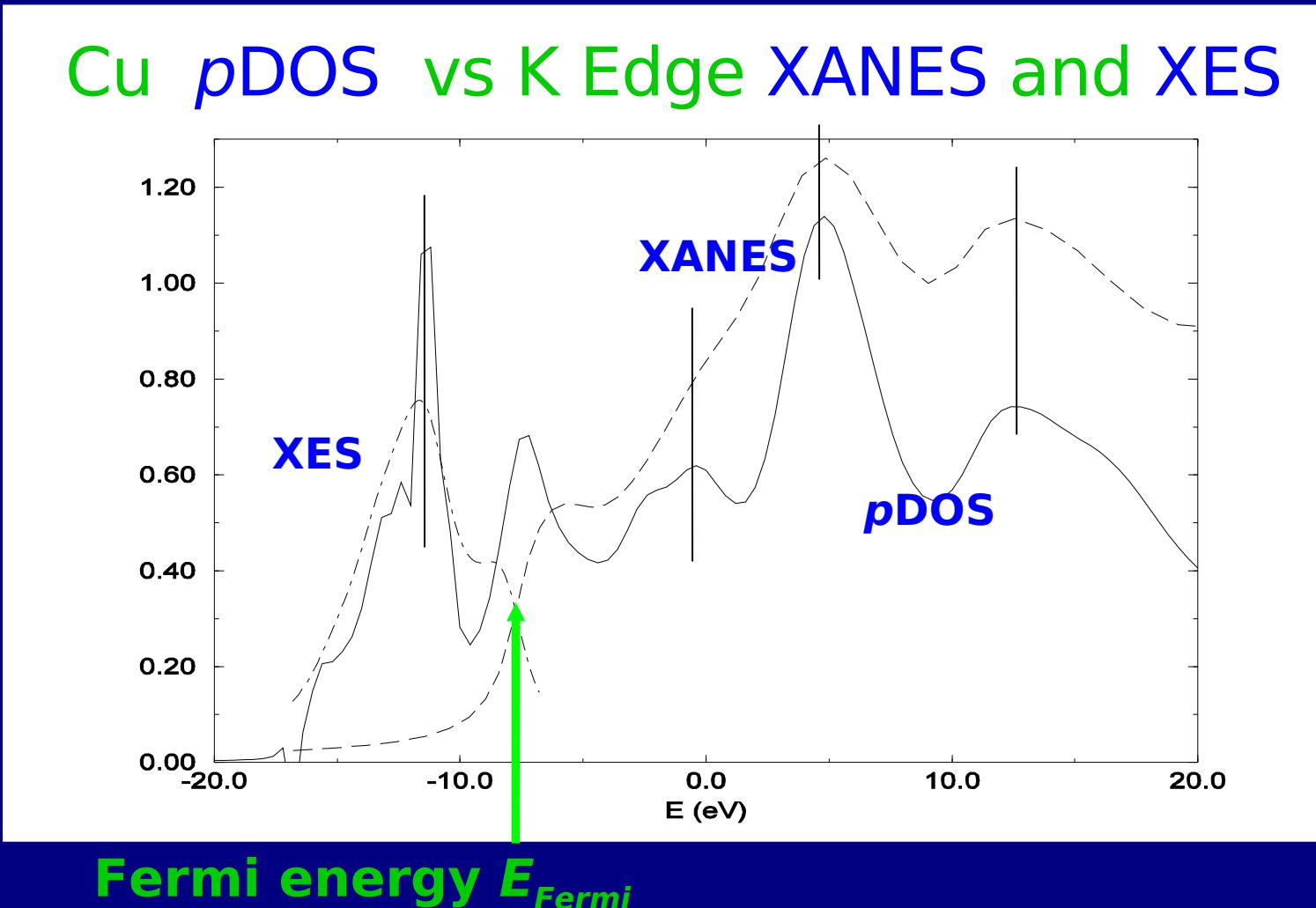
“Path expansion” – EXAFS eq.

6) $G(\omega) = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \dots$

$$= [1 - G_0 T]^{-1} G_0$$

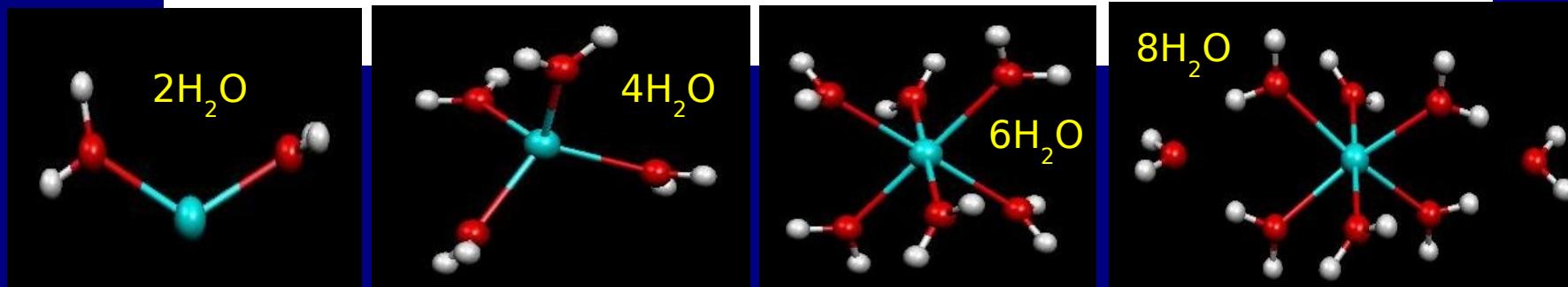
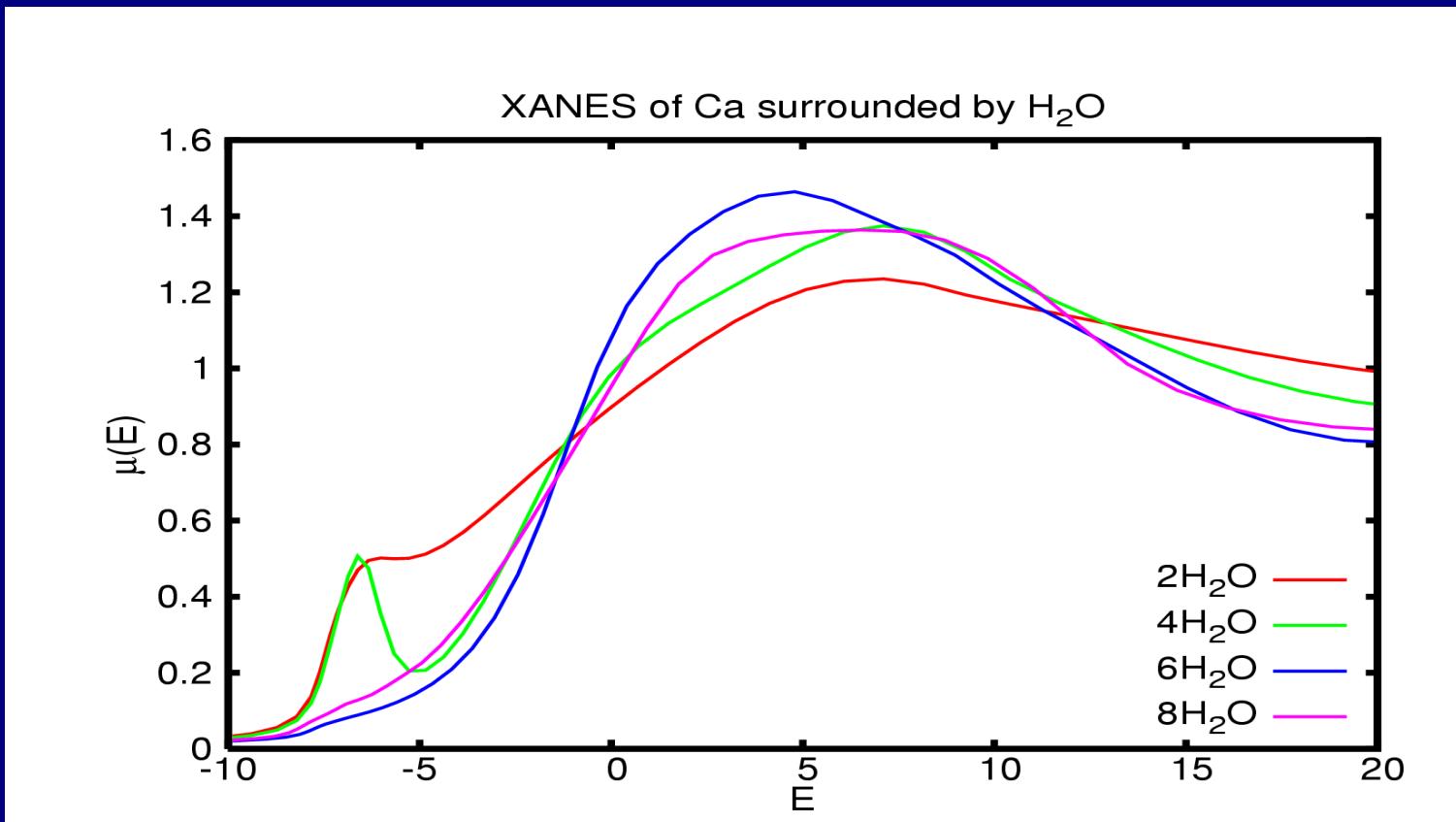
“Full Multiple Scattering”

XANES and LDOS



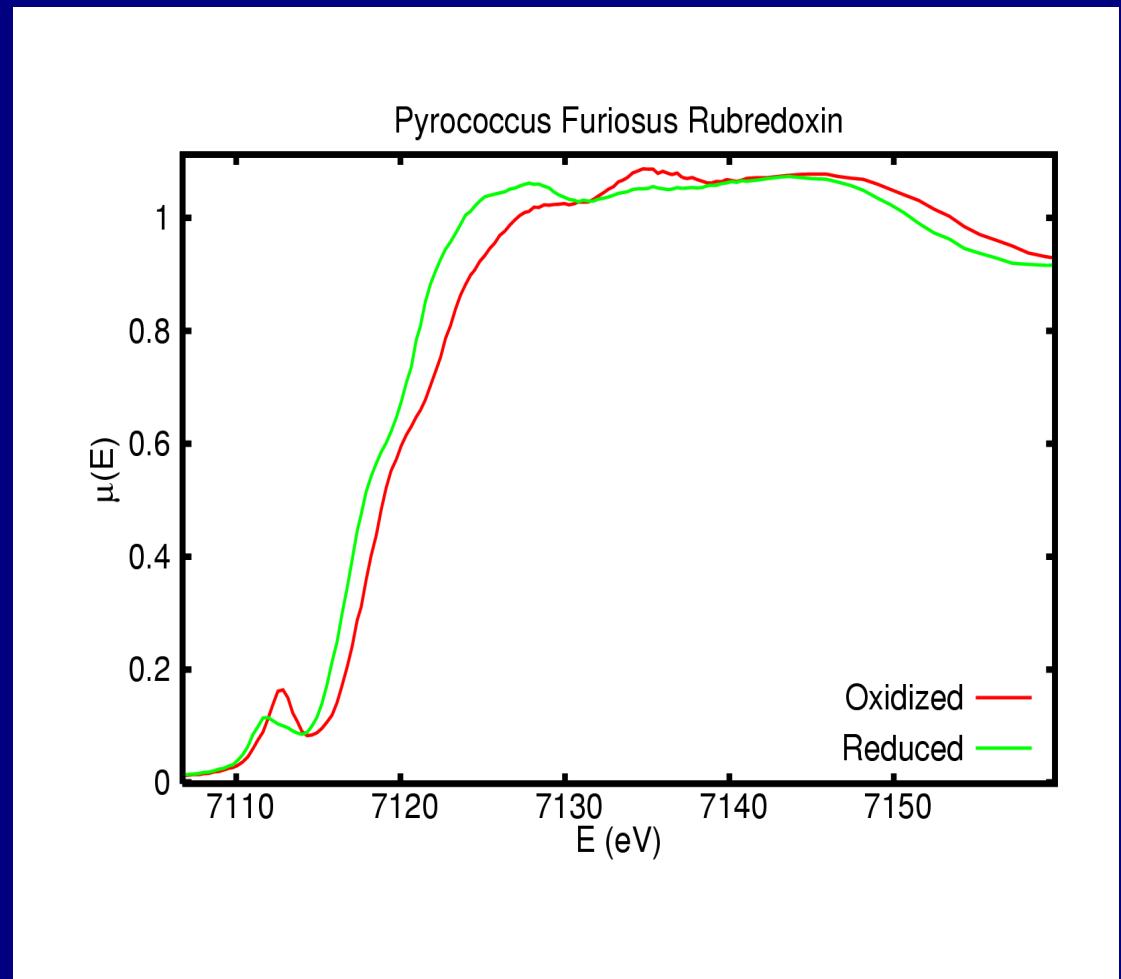
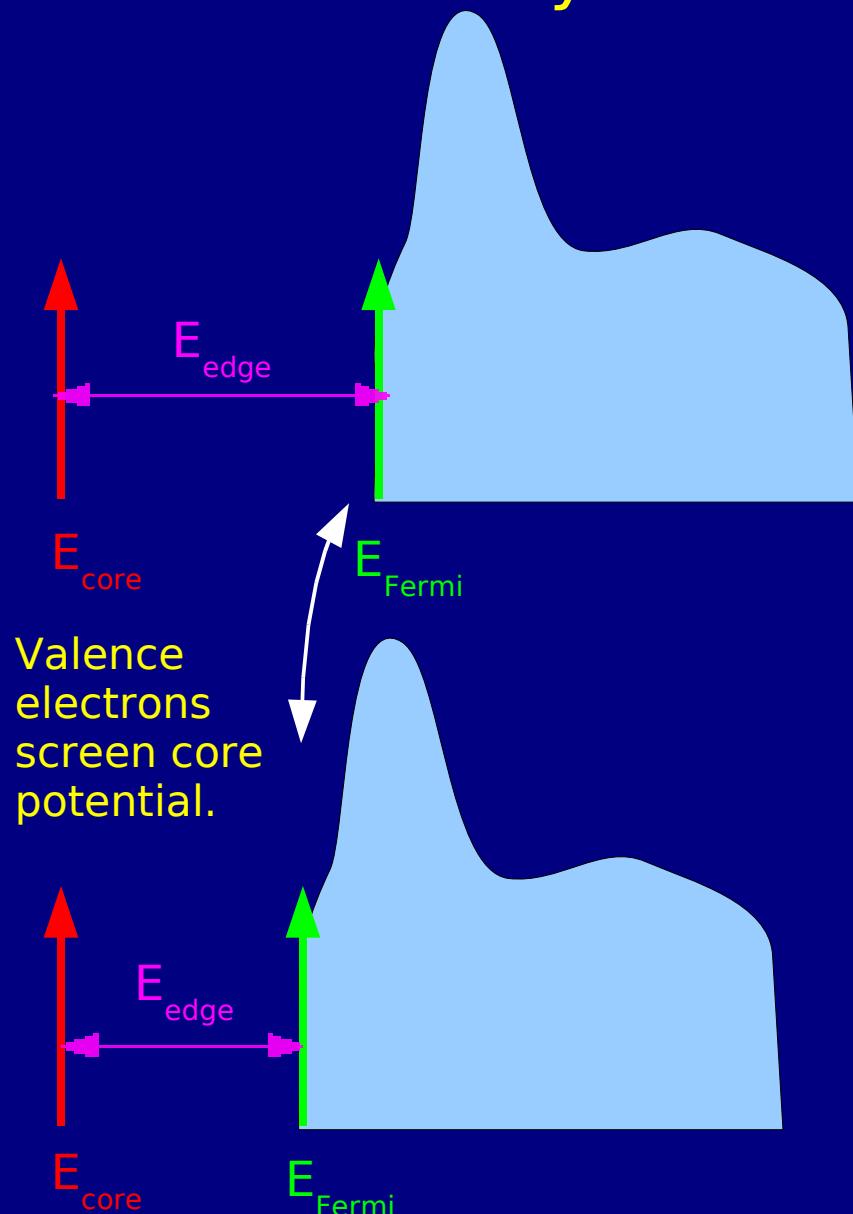
Symmetry and Pre/Near Edge Features

Sensitivity of XANES to Surrounding Geometry



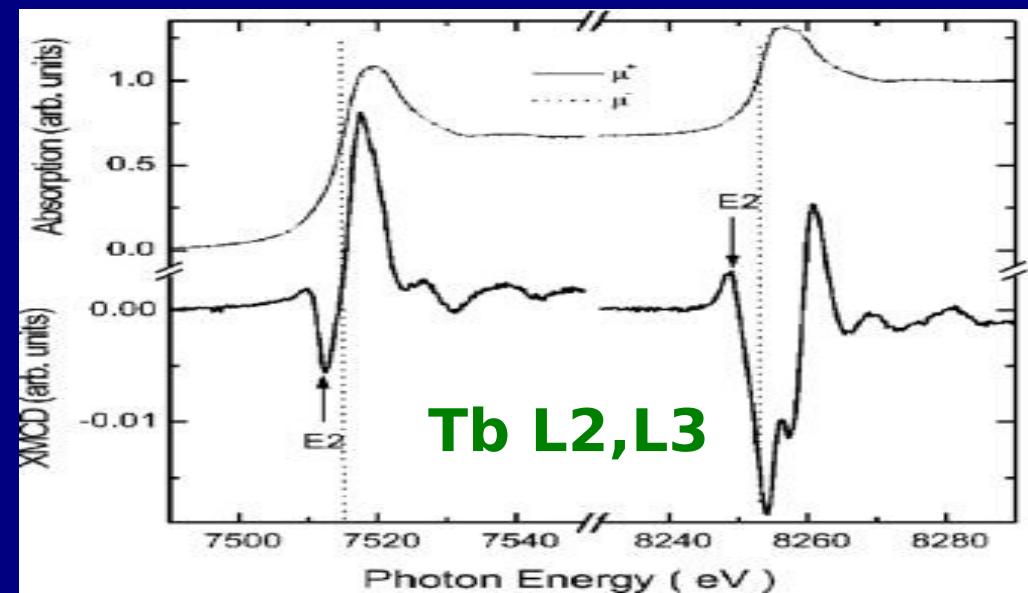
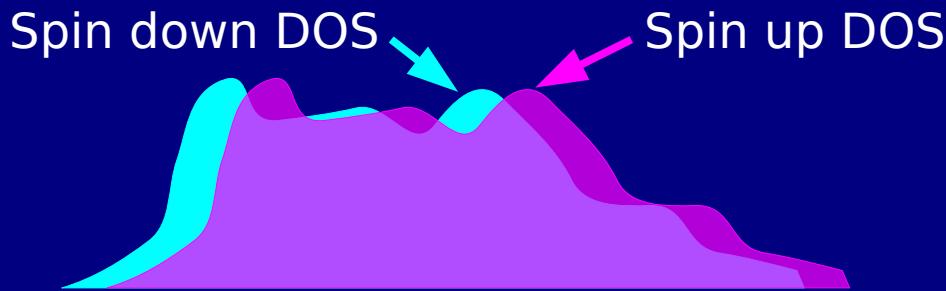
Edge Position and Charge Transfer

Sensitivity of XANES to formal oxidation state



L-Edges and XMCD

- Final states are s and d
- Spin orbit splitting gives splitting between L2 and L3 Edge
- XMCD – difference between absorption of left and right circularly polarized x-rays



Sum rules → Magnetic moments

Calculating XAS with FEFF

- FMS or Path Expansion?
- Calculation of EXAFS
- Calculation of XANES
 - Key features of FEFF8 for XANES
 - Convergence – FMS, SCF, Angular momentum basis
 - Possible failures of XANES calculations
 - Potentials
 - Treatment of the core hole
 - Self Energy and Many body effects

FMS or Path Expansion?

- Why not use FMS?
 - Conservative rule of thumb - FMS

$$k_{max} \approx \frac{l_{max}}{r_{mt}}$$

- Matrix size = $[N_{atoms} | l_{max} + 1)]^2$

$$k_{max} \gg \frac{1}{r_{mt}}$$

Computationally challenging

- Debye Waller Factors only correct for single scattering

When can we use Path Expansion?

- Terms in expansion must be “small”
 - Can happen in various ways
 - Back Scattering is small
 - 1) High k – large angle scattering is small
 - 2) Scattering potential is very weak
 - Large energy loss during propagation
 - 1) Inelastic mean free path is small
 - Debye Waller factors – DW factors tend to grow with pathlength
 - How do we know? Lanczos!

Calculation of EXAFS

- FEFF6 or FEFF8?
 - FEFF84 is here!
 - Relativistic
 - Self consistent potentials
 - FMS (XANES)
 - X-Ray Magnetic Circular Dichroism
 - Time-Dependent Local Density Approximation
 - FEFF6
 - Works well for most **EXAFS** applications
 - FEFF6L is FREE!

Calculation of XANES

- Structure – coordinates, species, vibrational character (phonon spectrum or Debye Waller factors/Debye Temperature)
- Convergence – FMS cluster size, SCF cluster size, Maximum angular momentum
- Important options for XANES
 - Self consistent potentials – Essential
 - Core hole treatment
 - Self energy

Potentials – Self consistency and core hole treatment

PHYSICAL REVIEW B

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Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure

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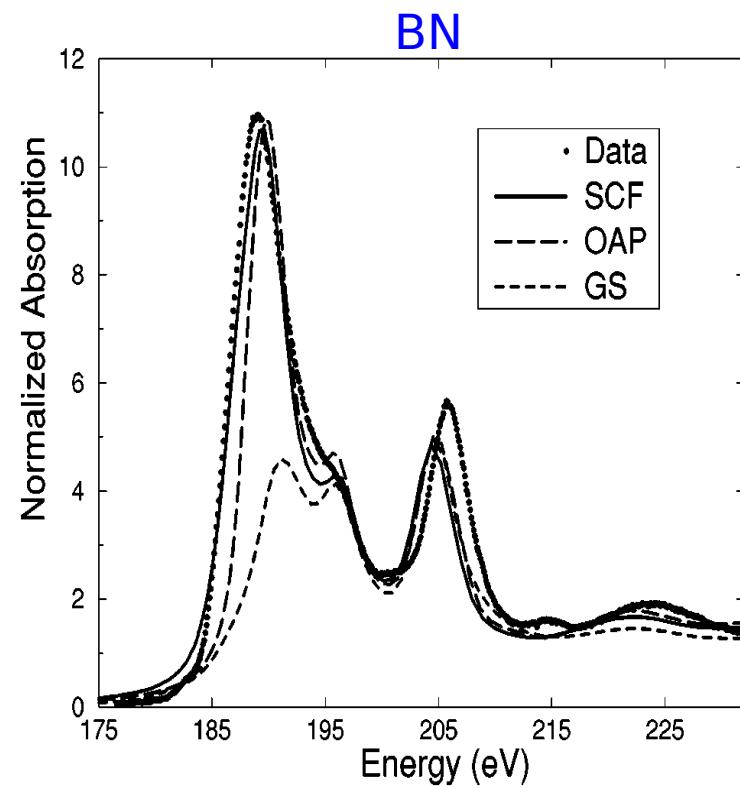
Department of Physics, University of Washington, Seattle, Washington 98195-1560

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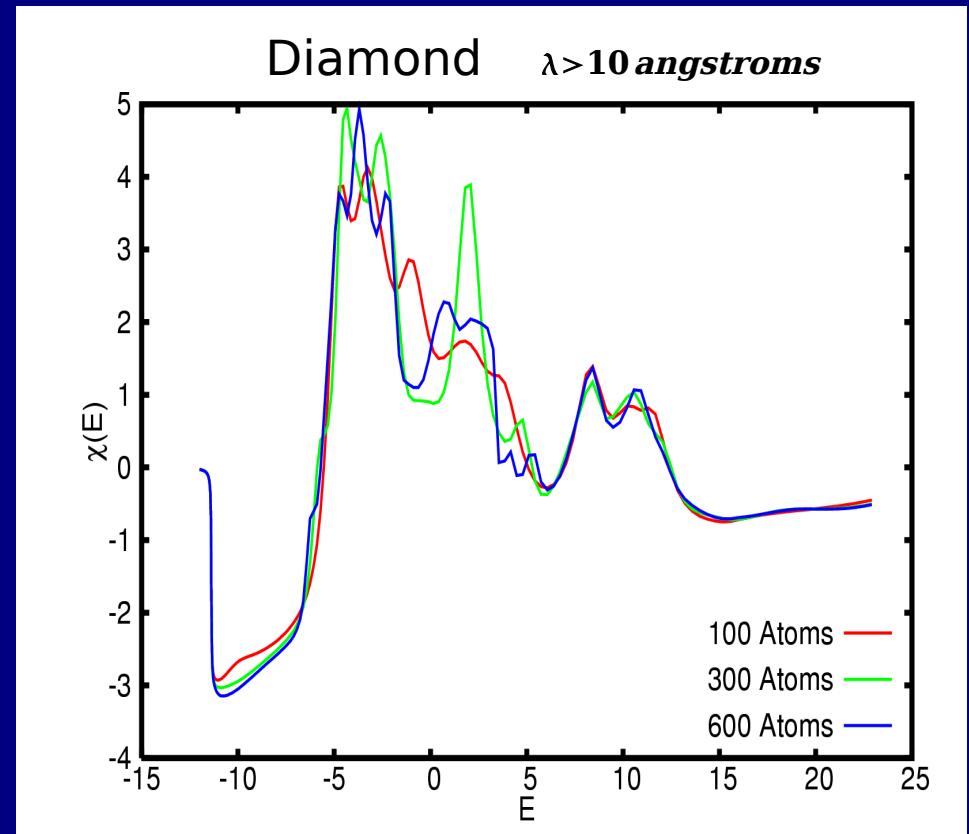
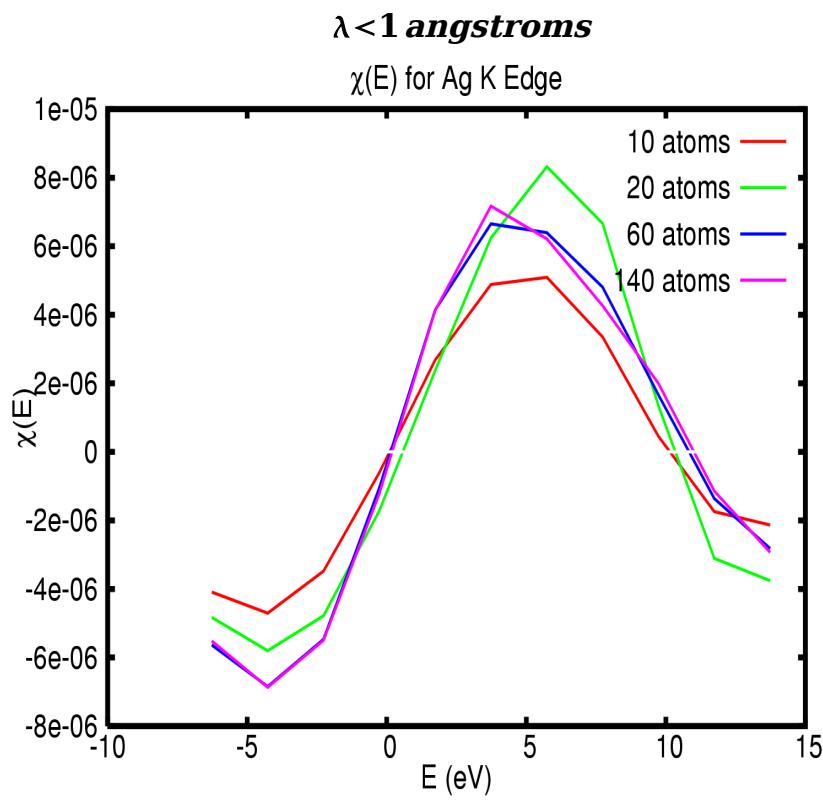
Core-hole, SCF potentials

Essential!

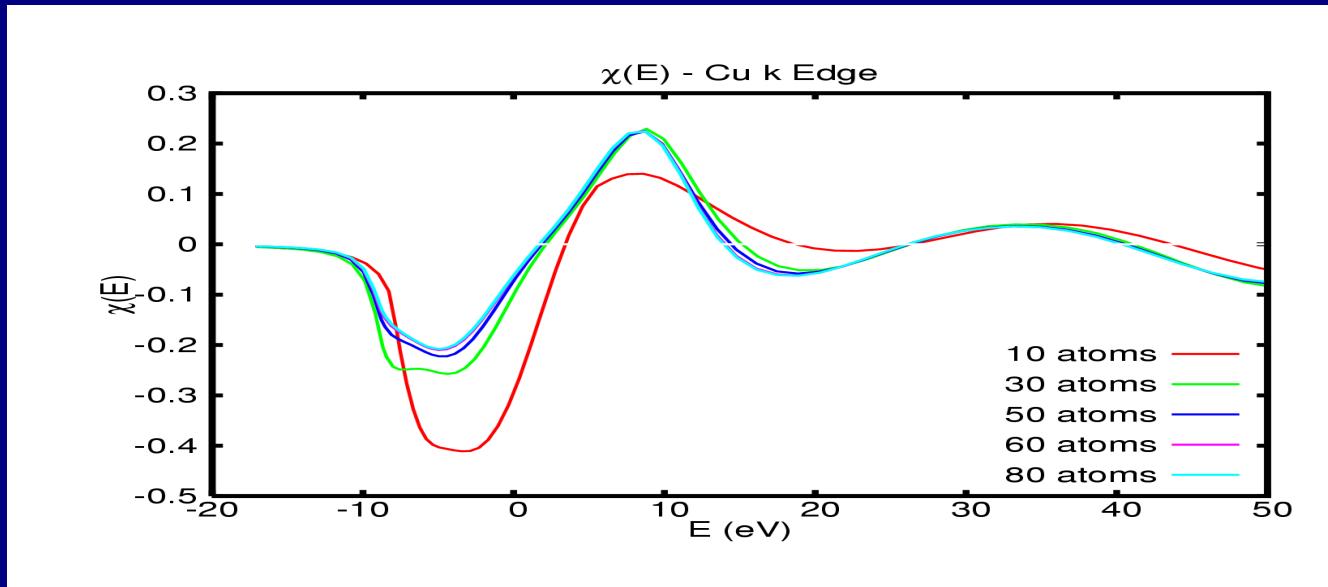


Convergence

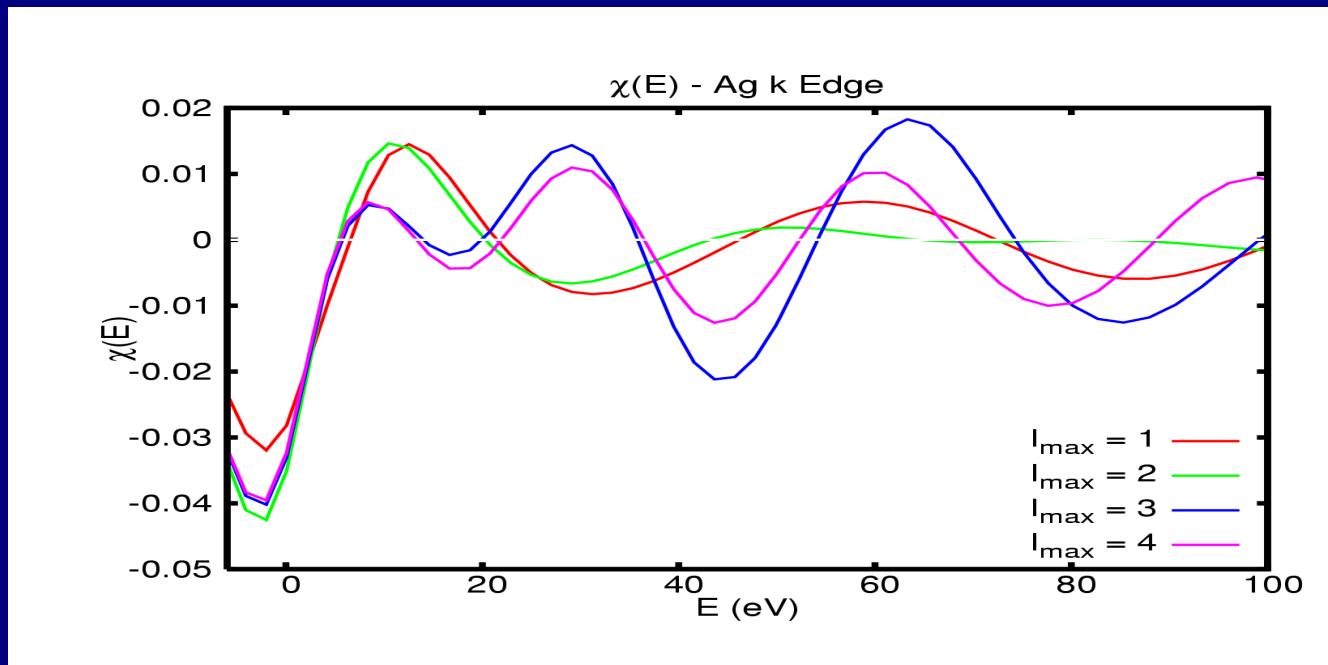
- FMS convergence – can guess order by inelastic mean free path λ



- SCF convergence ~50 atoms



- LMAX convergence $l_{max} \approx k_{max} r_{mt}$



When can I expect good agreement?

- Spherical Potentials
- Treatment of the core hole
- Self Energy
 - Metals – Hedin-Lundqvist self energy
 - Insulators – Hedin-Lundqvist or Dirac-Hara self energy
 - Molecules – Dirac-Hara or GS self energy
- Additional Many Body Effects

The Future of FEFF: FEFF9

- Full Non-Spherical Potentials
- Improved *ab initio* self energy
- Ab initio many body reduction factor (S_0^{-2})
- *Ab initio* Debye-Waller factors
- K-space formalism for crystals
- Improvement of the optical region
- Calculation of q-dependent x-ray Raman and EELS spectra
- GUI

Collaborators

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- **A. Nesvizhskii (UW)**
- **Y. Takimoto (UW)**
- **M. Prange (UW)**
- **Kevin Jorissen ()**
- **Timothy Fister (UW)**
- **E. Shirley (NIST)**
- **F. D. Vila (UW)**
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- **C. Bouldin (NSF)**
- **G. Hug (ONERA/CNRS)**
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- **S.R. Bare (UOP)**
- **H. Krappe (HMI)**
- **H. Rossner (HMI)**
- **L. Hedin**

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